

**Catalysts comprising metal compounds supported on a clay or hydrous silicate and their use.**

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**Abstract**

A catalyst which comprises a compound of a metal which is zinc, nickel, aluminium, copper, cadmium, cobalt, or magnesium, supported on a clay or a hydrous silicate, the catalyst being one which gives a minimum rate of conversion of 20% per hour at room temperature and atmospheric pressure of benzylchloride to diphenylmethane in a reaction mixture comprising benzene (140 ml), benzylchloride (10 ml), catalyst (8g at 1 m mol metal ion per gramme of catalyst). Such catalysts can be produced by contact of a solution of the metal compound with the clay or hydrous silicate. The catalysts may be used, for example, as alkylation or acylation catalysts.

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## Description

### CATALYST AND ITS USE

The present invention relates to a catalyst. It also relates to its use in chemical reactions. Such reactions include isomerisation and, particularly alkylation or acylation.

Many catalysts are known for use in alkylation (and similar reactions) of materials. Such materials may be open chain components or cyclic, and may be substituted. The materials may be based on hydrocarbon chains or may have atoms other than carbon in the backbone structure and thereby form heterocyclic rings. Particular materials which have been the subject of many publications, particularly patent specifications, include benzene. Benzene can be alkylated with benzylchloride to form diphenylmethane.

It has however been found difficult to achieve high yields of the desired product and to have a commercially worthwhile process in that the product can be easily recovered from the reaction mixture whilst also enabling the catalyst to also be separated and re-used.

EP-A- 0037628 discloses a process for the production of a diphenylmethane in which "a" benzene is reacted with "an" -chloromethyl benzene in the presence of sulphuric acid and a surfactant selected from particular classes. The surfactants include cationic surfactants which are stated to include phase transfer catalysts. Other surfactants which may be used are non-ionic surfactants which it is stated are believed to operate in the same manner as the cationic surfactants. When such a process was operated (as described in Example 12 thereof) using benzene, benzylchloride and 86% to 90% by weight sulphuric acid in a molar ratio of 10:1:2.5, with a phase transfer catalyst in an amount of 4% by weight with respect to the benzylchloride, and 1 hour reflux, a product is obtained in a yield of 85%. Other examples refer to substituted analogues and also to a wider range of acid strength and catalyst concentrations. However work-up appears difficult and involves dilution with water, separation, and further washing/neutralization before distillation.

US-A- 3 679 760 discloses a process for the preparation of diarylalkane which comprises reacting an alpha-haloalkylaromatic compound with an aromatic compound in the presence of a copper halide catalyst. In particular it refers to reacting benzene, with benzylchloride to form diphenylmethane. Whilst there is reference to reacting benzene benzylchloride and cupric chloride in a weight ratio of 1.8:1:0.33 ( a molar ratio of 3:1:0.30), there is little information on the yield or selectivity of the reaction. Indeed it is only stated that the presence of diphenylmethane was disclosed in the product by gas-liquid chromatography.

US-A- 3 678 112 is a similar disclosure to US-A- 3 679 760 but is concerned with alkylation or benzylation using an alkyl halide or a benzylic halide.

US-A- 4 251 675 is specifically directed to the preparation of a diphenylmethane compound by reacting benzene with a benzyl halide using ferric chloride as a catalyst, there being careful control of the ratios of the reactants and of the catalyst. There is only specifically disclosed a reaction of 1.2 mole of benzene with 0.4 mole of benzylchloride in the presence of 0.0002 mole of ferric chloride, the reaction being conducted at 65 DEG C for 2.5 hours. The yield would appear to be rather low and the selectivity was only 25%. Recovery would appear to require washing out of the catalyst which would not be filterable. The catalyst presumably could therefore not be re-used.

Laszlo and Mathy (Helv. Chim. Acta., 1987, 70, 577-586) report a transition metal ion exchanged montmorillonite. The best yield in the reaction of benzylchloride with benzene was obtained with a  $Ti^{(IV)}$  exchanged montmorillonite catalyst. The fastest reaction was with an  $Fe^{(III)}$  exchanged montmorillonite catalyst. In both cases reflux conditions were required, with a 1M solution of benzylchloride in benzene and 1g of catalyst. In the former case 66% diphenylmethane was obtained in 5 hours; and 57% in the latter. In both cases significant proportions of other products were obtained.

It has now been found possible to provide a novel catalyst whose use in chemical reactions, including isomerisation, and particularly alkylation and acylation reactions, overcomes the problems referred to hereinabove.

According to one embodiment of the present invention there is provided a catalyst, particularly an alkylation or acylation catalyst, which comprises a compound of a metal which is zinc, nickel, aluminium, copper, cadmium, cobalt or magnesium, supported on a clay or a hydrous silicate, the catalyst being one which gives a minimum rate of conversion of 20% per hour at room temperature and atmospheric pressure of benzylchloride to diphenylmethane in a reaction mixture comprising: benzene (140 ml), benzylchloride (10 ml), catalyst (8g at 1 m mol metal ion per gramme of catalyst).

The term "clay" is unusual in that it has decidedly different meanings to technologists in different fields. A definition which seems to be particularly applicable to the clay supports which may be used in the present

invention is that in the Penguin Dictionary of Science, namely "finely divided rock materials whose component minerals are various silicates, mainly of magnesium or aluminium". Another definition, frequently used by chemists is "a naturally occurring sediment (including that obtained by alteration in situ by supergene and hydrothermal processes) or sedimentary rock composed of one or more minerals and accessory compounds, the whole usually being rich in hydrated silicate of aluminium, iron or magnesium, hydrated alumina, or iron oxide, predominating in particles of colloidal or near-colloidal size, and commonly developing plasticity when sufficiently pulverised and wetted" (see Kirk-Othmer, Encyclopaedia of Chemical Technology, Volume 5, page 544, 2nd edition, John Wiley and Sons, Inc., New York, New York 1964).

Especially useful clays have been found to be the "montmorillonite" clays. The "montmorillonite" clays refer generally to crystalline clays having three layers. These clays are composed of units having two layers of silica tetrahedrons and one centrally disposed dioctahedral or trioctahedral layer. Such montmorillonite clays may be classified as either having an expanding lattice structure or a non-expanding lattice, (see The Encyclopaedia of Chemistry, third edition, Van Nostrand Reinhold Co., New York, 1973). Chemically, they may be considered to be clays of the general formula  $\text{HA}(\text{Si}_2\text{O}_6)_n$  but with variable A:Si ratios, variable amounts of water and usually containing variable amounts of exchangeable cations.

The term "montmorillonite" has also been used to specify a species member of the "montmorillonite" genus: i.e. an aluminous member of the group accorded the empirical Formula

Both bentonite and hectorite are members of the expanding lattice montmorillonite subgenus. One difference between the two is that in hectorite the aluminium present in the bentonite lattice is almost completely substituted by magnesium atoms. Another difference is that lithium and fluorine are absent from the bentonite lattice and present in the hectorite lattice. Bentonite may be characterised as a sodium aluminium silicate, with hectorite being a sodium magnesium-fluor-litho silicate.

The hydrous silicates which may be employed are usually aluminium silicates with continuous sheet structures.

A first method of preparing the catalyst comprises firstly preparing a solution of a compound (for example salt) of the relevant metals (as defined hereinabove) followed mixing the clay or hydrous silicate with the solution (usually by stirring the solution in the presence of the clay), and preferably then slowly evaporating the solvent. However the catalyst may be filtered from solvent (and the solvent then preferably evaporated therefrom) or even used without separation of the catalyst from the solvent.

A second (alternative) method of preparing the catalyst is to first wash or stir the clay with a solution of the metal compound (for example metal salt) until no further iron (iron being originally present in the clay) is removed into the solvent. The resulting ion-exchanged clay can then be treated as in the procedure above.

Since the concentration of the metal compound in the solution changes during the preparation of the catalyst due to evaporation, the concentration used is not of importance. Any concentration can be used bearing in mind the amount of solid and the size of the vessel in which the catalyst is being prepared, together of course with the solubility of the particular salt. However it is preferred to use concentrations close to saturation so as to have less solvent to subsequently remove.

The compound of the metal is usually a salt. Examples of suitable salts are nitrates, phosphates, sulphates and, particularly halides. Whilst the halides may be iodides or bromides, the chlorides are preferred. Particularly useful chlorides are zinc chloride, nickel chloride, cupric chloride and magnesium chloride. The metal may however be present in the anion rather than in the cation as in the salts particularly disclosed herein. The particularly preferred metals are zinc and nickel.

The solvents usually employed are selected from alcohols, particularly methanol. It is necessary to bear in mind the restricted solubility of the metal compounds.

Zinc chloride and clay form particularly useful catalysts. A particular catalyst (which we refer to as "clayzic") can be prepared by stirring a solution of zinc chloride in methanol containing clay in accordance with the first method as described above. The methanol can then be removed by evaporation. A corresponding catalyst prepared in accordance with the second method as described above is one which we refer to as "clayzicic".

The loading of the metal compound onto the clay is usually in the range of 0.1 to 20 m mol of metal compound per gram of clay, preferably 0.2 to 2 m mol per gram, and more preferably about 1 m mol per gram.

The catalyst so produced may then be activated by heating, usually at a temperature in the range of 50 DEG C to 300 DEG C. A separate activation step may not be required, particularly when solvent is stripped since such stripping usually involves heating to evaporation and that heating leads to activation.

According to another embodiment of the present invention there is provided a process for the production of an organic compound (for example an isomerised, alkylated or acylated compound) which comprises reacting an organic substrate with a suitable agent (for example an isomerising agent, an alkylating agent or an acylating agent) in the presence of a catalyst which comprises a compound of zinc, cadmium, nickel, copper, magnesium, aluminium or cobalt supported on a clay or hydrous silicate. The catalyst is as more particularly described hereinabove.

The organic substrate may be a straight chain or branched hydrocarbon compound. However it may also be a cyclic structure which is carbocyclic or heterocyclic.

Examples of suitable organic substrates which may be used in the process of the present invention include those compounds having the general formula where R<1> to R<6> may independently each be

- (a) H, D (deuterium), F, Cl, Br, I;
- (b) alkyl;
- (c) OR;
- (d) SR;
- (e) NR<7>R<8>
- (f) COR
- (g)
- (h)
- (i) C = C - R
- (j) CN
- (k) NO<sub>2</sub> wherein R and R<7> to R<1><1> may independently each be H, D, alkyl, aryl or acyl which may be substituted; and Y may be O, NH, ND, NR (wherein R is as defined above) or S.

Any two substituents may be joined to form a ring, which in turn may be substituted.

Suitable alkylating or acylating agents which may be used in the process of the present invention include

- (1) R<1> R<2> R<3> CX<1>
- (2) R<1> R<2> C = CR<3> R<4>
- (3) R<1>C = CR<2>
- (4) R<1> R<2>
- (5) RCOX<2>
- (6) RCHO
- (7) R<1> COR<1> wherein R and R<1> to R<4> independently each as defined hereinabove for the organic substrates,

X<1> is F, Cl, Br, I, o-tosyl, OH or OR (R being as hereinabove defined), and

X<2> is F, Cl, Br, I, OH, OR or @CR (R being as hereinabove defined).

The substance to be alkylated or acylated (the substrate) is reacted with the alkylating agent or acylating agent in the presence of a catalyst. The molar ratio of reactants is usually (agent:substrate) in the range 1:20, preferably 1:5 to 1:10, particularly when an alkylating agent is being used. However, for acylating agent the ratio is close to 1 and may be even be less than 1 for some systems.

The amount of catalyst employed ranges widely depending on the particular catalyst and the reactants. Whilst it may be within the wide range of 0.1% to 100%, it is usually 0.1% to 10% for alkylation reactions. However for acylating reactions it is usual to employ a larger amount of catalyst, even approaching 100% (with respect to the acylating agent being used), that is close to a ration of 1:1. The percentages are based on the alkylating/acylating agent.

The temperature at which the alkylation or acylation is conducted usually depends on the particular reaction but is generally in the range of 0 DEG C to 200 DEG C.

Whilst the alkylating agent or acylating agent may be added slowly to the reaction medium, it may be added totally at the commencement. The reaction medium may also contain a solvent. The solvents which may be employed include saturated hydrocarbons, aromatic hydrocarbons of lower activity than the substrate, and chlorinated hydrocarbons, such as, for example, chloroform. However the substrate itself may act as the solvent.

It is also possible to conduct the process under ambient or elevated pressure.

On completion of the reaction the catalyst may be filtered from the reaction medium and re-used. Purification and isolation of the product may be performed in a conventional manner.

The ability to recover the clay supported catalyst is an important advantage of the present invention. In comparing the present process with that disclosed in EP-A- 0037628 it has been found that whilst a similar rate of reaction occurs and the present process have a very slightly lower conversion, the working up of the

product (involving filtration) is much easier. In contrast, in the process of EP-A- 0037628 the phase transfer catalyst is lost as is presumably the sulphuric acid unless detailed steps are taken for the re-cycling of the acid. Further catalysts within the scope of the present invention can be much more powerful than the phase transfer catalysts used in EP-A- 0037628. For example, zinc chloride or nickel chloride supported on clay enable complete reaction of benzene with benyl chloride to be obtained in only 15 minutes at a temperature as low as 20 DEG C.

In connection with US-A- 3 679 760 referred to hereinabove it is believed that the mentioned ratios of reactants and catalyst give poor selectivity. Whilst it may be that in the process the catalyst, which is present in considerable amounts, could be filtered off, there is no disclosure as to the possibility of it being re-usable. It will be noted that reaction times (11 hours) and high temperatures (90 DEG C) are employed that for the corresponding aspects of the present invention. Furthermore the present invention employs considerably less catalyst (and even that amount is re-usable) whilst producing a faster reaction.

As mentioned above, the catalysts employed in US-A-4 256 675 presumably cannot be re-used. We have attempted to reproduce the process of that specification but problems arose in the washing stage in respect to attempted separation since emulsions formed which separated only very poorly so leading to loss of product, as well as discolouration.

The present invention will now be further described with reference to the following Examples, but is in no manner limited thereto.

#### Example 1

Reaction of benzene and benzylchloride in the presence of zinc chloride supported on montmorillonite-K10 was conducted as follows. A catalyst was prepared by dissolving 10 m mol of zinc chloride in 250 ml of methanol. 10g of the clay were added, and the mixture stirred. The methanol was then removed using a rotary evaporator. The catalyst so produced (clayzic) was then heated in an oven at 170 DEG C for 18 hours. 8g of this catalyst were then added to a solution of benzylchloride (10 ml) in benzene (140 ml), and the mixture stirred at room temperature. After 15 minutes 99% conversion of the benzylchloride to diphenylmethane was achieved. Three further additions of benzene and benzylchloride were made, with conversion in each case being in excess of 90%.

#### Example 2

Reaction of benzene and benzyl chloride in the presence of copper II chloride supported a montmorillonite K10 was conducted as follows. Example 1 was repeated using the same reaction conditions but with copper (II) chloride in place of zinc chloride. After one hour, 52% conversion of benzyl chloride was achieved.

#### Example 3

The procedure of Example 1 was repeated, but using zinc bromide in place of zinc chloride. After 1 hour 95% conversion of benzylchloride was achieved.

#### Example 4

The procedure of Example 1 was repeated, but using zinc iodide in place of zinc chloride. After 15 minutes, 91% conversion of benzylchloride was achieved.

#### Example 5

The procedure of Example 1 was repeated, but using nickel chloride in place of zinc chloride. After 15 minutes, 96% conversion of benzylchloride was achieved.

#### Example 6

The procedure of Example 1 was repeated, but using zinc nitrate in place of zinc chloride. After 1 hour, 60% conversion of benzylchloride was achieved.

#### Example 7

The procedure of Example 1 was repeated, but using zinc sulphate in place of zinc chloride. After 1 hour, 30% conversion of benzylchloride was achieved.

#### Example 8

The procedure of Example 1 was repeated, but using zinc phosphate in place of zinc chloride. After 15 minutes, 66% conversion of benzylchloride was achieved.

#### Example 9

Reaction of benzene and paraformaldehyde in the presence of zinc chloride and montmorillonite K10 was conducted as follows. A catalyst was prepared by dissolving 20 m mol of zinc chloride in 200 ml of methanol. 20g of the clay were added to this solution and the mixture is stirred for 15 minutes. The solids were then separated by filtration and added to a second zinc chloride solution (as before).

This mixture was then stirred and filtered as before. The procedure was repeated until no iron ions could be detected in the methanolic filtrate solution. 10g of the ion exchanged clay, thus prepared, were then added to a solution of 10 m mol of zinc chloride in methanol, and the solvent removed by evaporation as in Example 1. The catalyst thus prepared was referred to as clayzicic.

10g of clayzicic were added to 170 ml of benzene and 2.5g of paraformaldehyde, and the mixture was then stirred at 80 DEG C. Three further quantities of 2.5g of paraformaldehyde were added to the reaction mixture hourly.

After 5 hours, 11.5g of diphenylmethane were produced.

#### Example 10

Reaction of benzene and sec-butylchloride in the presence of clayzic (produced as in Example 1) was conducted as follows. 60g of benzene and 11g of sec-butylchloride were stirred with 1g of clayzic at 80 DEG C. After 4 hours 12g of sec-butylbenzene were formed.

#### Example 11

Reaction of benzene and benzhydrol in the presence of clayzic (produced as in Example 1) was conducted as follows. 150 ml of benzene and 15g of benzhydrol were stirred with 3g of clayzic at 80 DEG C for 2 hours. The conversion of benzhydrol was 69% triphenylmethane, 13% diphenylmethane and 13% benzophenone.

#### Example 12

Reaction of benzene and benzoylchloride in the presence of clayzic (produced as in Example 1) was conducted as follows. 90 ml of benzene and 12g of benzoylchloride were stirred with 10g of clayzic at 83 DEG C. After 40 hours 30% of the benzoylchloride was converted to benzophenone.

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